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(54) Title: PESTICIDAL PRE-TREATMENT OF WOOD BY MICROEMULSION, MICELLAR OR MOLECULAR SOLUTION

## (57) Abstract

Timber can be preventatively treated against pests with a pesticidal formulation which comprises a microemulsion, micellar solution or molecular solution, whose average particle or droplet size is less than 200 nm. Pesticides such as pyrethroid insecticides/acaricides (for example permethrin) and/or fungicides (for example IPBC and/or propiconazole) can be present in the formulation. The formulations contain water, and so are in improvement on solvent-based systems; in spite of their water content, their ability to penetrate timber is at least as good as, and even better than conventional solvent formulations.

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PESTICIDAL PRE-TREATMENT OF WOOD BY MICROEMULSION,  
MICELLAR OR MOLECULAR SOLUTION.

5 This invention relates to the treatment of wood and products containing wood for the purpose of preservation against pests. The invention has particular application in the pre-treatment of timber for structural use, for example in buildings, among other applications.

10 Many of the most useful pesticides for the treatment of timber are not water soluble. One such group of compounds are the pyrethroids. Typical solvents used for pyrethroids include hydrocarbons such as xylene, heavy aromatic naphtha, kerosene and various paraffins or alkanes. Many agents for use against plant timber pests  
15 such as fungus, mould, lichen and algae are also insoluble in water and have conventionally to be formulated in organic solvents.

20 Timber treatment is one of the most important markets for pesticides. Timber, particularly softwood timber in temperate climates, is widely used structurally; and it is clearly important that its life is not unnecessarily shortened by insect, acarine, fungal or other pests. Important insect or acarine pests for timber include but  
25 are not limited to the common furniture beetle (*Anobium punctatum*), other wood-boring beetles such as the house longhorn beetle (*Hylotrupes bajulus*), and the termite (*Reticulotermes santonensis*). Important fungal pests for timber include, but again are not limited to, dry rot (*Serpula lacrymans*), the various forms of rot known  
30 colloquially as wet rot, including brown rot (*Coniophora puteana*) and white rot (*Polystictus* (*Coriolus*) *versicolor*), and the various fungal stains such as bluestain (stain in service) and sapstain. Other plant

pests include moulds (such as *Aspergillus* spp., *Penicillium* spp., *Paecilomyces* spp., *Alternaria* spp. and *Cladosporium* spp.), lichen and algae.

5 The timber treatment market can be conveniently be  
divided into the preventative or pre-treatment segment  
and the remedial or post-treatment segment. The pre-  
treatment market treats timber, before it is sold or  
distributed for construction or other applications, for  
10 the purpose either of conferring long term protection  
during service or for short term protection during  
storage and transport. The post-treatment market treats  
timber which has previously been installed and has  
become, or is at risk of becoming, infested. It is with  
15 the pre-treatment market that the present invention is  
particularly concerned.

Pesticidal timber pre-treatment is generally carried out  
by a double vacuum process to aid penetration of the  
20 pesticide into the bulk of the timber. For example, in  
the UK, timber pre-treatment is generally undertaken by  
a double vacuum immersion pre-treatment system in  
accordance with the prevailing relevant British Standard,  
currently BS 5589:1989 for pine. The pesticide or  
25 pesticides (often a mix of insecticide/acaricide such as  
permethrin and a fungicide such as propiconazole and/or  
IPBC) is conventionally formulated in a light organic  
solvent such as white spirit or toluene.

30 Solvent based systems such as these have many  
disadvantages. First, there is the real and obvious risk  
of fire. Secondly, organic solvents pose a health hazard  
for the operators of the pre-treatment system. Thirdly,  
the smell of organic solvents, even at levels below those

which are health-threatening, can be offensive. Fourthly, although solvent recovery systems may be in operation, there will inevitably be some loss, not least because the pesticidal solution penetrates into the wood: solvent loss can be costly both in terms of its impact on the environment and in terms of cash.

For some years, therefore, the search has been on to develop a timber pre-treatment system which represents an alternative to the wholesale use of organic solvents. Formulating water-insoluble pesticides as emulsions has been looked at both in the timber treatment industry (although hitherto in the post-treatment segment) and in other areas, such as in agricultural and public health applications. Microemulsions represent a more recent approach. WO-A-8807326 discloses improved pesticidal activity for various microemulsion and related formulations (including micellar solutions) having a relatively high water content. WO-A-9003112 discloses that such microemulsion and related formulations can be used to treat wood or timber and details various advantages resulting from the formulations' use on timber *in situ*.

The use of emulsions in particular, and water-containing two-phase formulations in general, in the timber pre-treatment market does not seem to have generated much enthusiasm, if indeed it has ever been suggested. Possibly this is because of bad experiences that those working in the area have had with water-containing pesticidal formulations. For example, Berry and Orsler, in the *Building Research Establishment Information Paper IP 15/83* (October 1983), said:

The ability of emulsion systems to penetrate wood is unlikely to be improved by altering the formulation. Since the emulsions consist of oil droplets dispersed in a continuous water phase,  
5 it is essentially the water that determines the basic physical properties of the systems, and water does not penetrate wood well.

And Saunders and Blow, among many comments denigrating the use of water-based two-phase formulations in timber treatment in the *Record of the 1985 Annual Convention of the British Wood Preserving Association* at pages 64 to 73, said:

15 Whilst water borne preservatives did not have these drawbacks [ie, colour and odour], they did not penetrate the timber to any appreciable depth when applied by brush or spray;

20 and

Adequate penetration is a "holy grail" of timber preservation and its importance has been stressed in many publications;

25 and

Therefore it appears possible, indeed, almost inevitable, that unless a substantial external pressure can be applied, the flow of an emulsion into timber will be poorer than the flow of a simple water borne preservative. Moreover, there appears to be a real possibility that the oil phase of an emulsion  
30

(which is the carrier for the timber preservative chemicals) may be filtered out in the most superficial layers of the timber.

5 In summary, although the disadvantages of solvent-based systems are known, it has been thought that there is no practical alternative to their use in timber pre-treatment; two-phase water based systems have not been  
10 believed capable of fulfilling the need for an alternative, not least because of their worse penetrative ability.

Remarkably, it has now been found not only that are  
15 certain water-containing formulations effective for timber pre-treatment but also that the use of these formulations can actually result in better pesticidal penetration into timber and better loading of the pesticide at a given depth. The formulations in question are microemulsions and related formulations, as disclosed  
20 in WO-A-8807326 and WO-A-9003112.

According to a first aspect of the present invention, there is provided the use of a pesticidal formulation which comprises a microemulsion, micellar solution or  
25 molecular solution, whose average particle or droplet size is less than 200 nm, in the pesticidal pre-treatment of timber.

Microemulsions and micellar solutions are preferred for  
30 use in the invention. The droplet or particle size is usually the Z average mean size, which can be defined as the model free mean of light scattering (for example at 90°) and measured with a MALVERN AUTOSIZER™ IIc laser particle sizer.

In contrast to microemulsions, macroemulsions (which would result from the dilution with water of an emulsifiable concentrate) appear white or opaque and are characterised by their property to separate into their two original liquid phases on standing; the average particle diameter will generally be above 200 nm. Microemulsions and micellar solutions are translucent and do not separate. Microemulsions can be considered as having average droplet (or particle) diameters of from 10 to 200 nm, micellar solutions as having average particle diameters of from 2 nm to 10 nm and molecular solutions as having average particle diameters of less than 2 nm. Recent evidence, however, does suggest that microemulsions with droplet diameters below 10 nm are possible.

Formulations useful in the invention are generally as described in WO-A-8807326 and WO-A-9003112, and the generalisations and preferences set out in those two publications in relation to the formulation details generally apply to the present invention. The contents of WO-A-8807326 and WO-A-9003112 are incorporated herein by reference. Microemulsion and related formulations containing a surfactant which markedly lowers the surface tension of water (or, in other words, a wetting agent) may also be useful in this invention; such formulations are disclosed in WO-A-9003111, the contents of which are again incorporated herein by reference.

As with macroemulsions, microemulsions can be of the water-in-oil (w/o) or oil-in-water (o/w) type and can be made to invert from one to another. In the area of inversion, microemulsions display peculiar properties. Starting from fluid w/o microemulsions, as water is



added, they pass through a viscoelastic gel region and as more water is added they invert to a fluid o/w microemulsion. This process is reversible and the viscoelastic gel region (which can be almost solid) comprises a hexagonal array of water cylinders adjacent to the w/o stage and a lamellar phase of bimolecular leaflets adjacent the o/w stage. These phases of the gel stage are liquid crystalline phases. In the present invention, the formulations used will generally be o/w.

Pesticidal formulations useful in the invention will generally comprise water, oil, a surfactant and a cosurfactant.

As indicated above, if the formulation is a microemulsion, the microemulsion will generally be clear or translucent, except in the viscoelastic gel phase. Micellar solutions and molecular solutions may additionally be clear.

The water can be tap water, although distilled water can be used. The amount of water in the microemulsion will depend on many factors but typically for w/o microemulsions will be from 20 to 70% w/v and for o/w microemulsions it shall be from 40 to 95% w/v. Some hardness in the water, although not essential, may in practice be beneficial. Between 100 and 200 ppm hardness (as  $\text{CaCO}_3$ ) may be appropriate, particularly around 150 ppm or 160 ppm. Calcium ions may be provided by other calcium salts, such as calcium chloride. Potassium or other metal ions may be present, as they appear to have a stabilising effect on droplet size.

The oil need not merely be an "oil" in the sense of a petroleum fraction, although such oils are included; the term "oil" is used to mean any non-aqueous solvent in which a substance of interest is soluble and which is immiscible with water; alternatively, the substance of interest may itself be the oil. Having said that, the oil may be animal, vegetable, mineral or silicone or some other organic solvent which is water-immiscible, such as an optionally halogenated hydrocarbon. The hydrocarbon may be aliphatic or aromatic or have both aliphatic and aromatic moieties. Typical solvents include xylene, naphthalene, kerosene, isoparaffins and halogenated hydrocarbons. Many of the proprietary hydrocarbon solvents sold under the trademarks SHELLSOL and SOLVESSO are suitable. Some oils impart a pleasant odour to the formulations: pine oil is an example.

The surfactant may be any typical emulsifier as found in most macroemulsion systems. The surfactant may be anionic, cationic, zwitterionic or nonionic. Anionic surfactants are more frequently used. Suitable anionic surfactants include hydrocarbon sulphates, sulphonates and sulphamates, especially compounds wherein the hydrocarbon moiety is an alkyl or alkylaryl group. Soaps (hydrocarbyl carboxylates) can also be used, as can sulphocarboxylic acids such as sulphosuccinic acid. Examples of specific anionic detergents that can be used include alkyl benzene sulphonates and sulphonic acids such as C<sub>8</sub> to C<sub>16</sub> alkyl benzene sulphonates and sulphonic acids including dodecyl benzene sulphonic acid (a predominately straight chain mixture of which compounds is sold under the trade mark NANSA SSA). Other suitable alkyl benzene sulphonic acids include those sold under the trade mark MANRO BA by Manro Chemicals.

The selection of an appropriate surfactant can be made by one of skill in the art without undue experimentation. As a guiding principle, it should be borne in mind that it is highly preferable to match, in a chemical sense, the structure of the surfactant with the structure of the oil. For example, if the oil is aromatic, such as xylene or naphthalene, it is preferred to use a surfactant having an aromatic moiety, for example an alkyl benzene sulphonate or an alkyl naphthalene sulphonate. If the oil is aliphatic, an aliphatic surfactant is preferred such as an alkyl sulphonate or a dialkyl sulphosuccinate (such as dioctyl sulphosuccinate) or a soap. Another factor in determining the choice of surfactant is the type of microemulsion (w/o or o/w) to be produced. Low HLB surfactants (for example having an HLB of from 4 to 9, particularly 4 to 7) tend to stabilise w/o microemulsions and should therefore for preference be used for w/o microemulsions and high HLB surfactants (for example having an HLB of from 9 to 20, particularly 9 to 20) tend to stabilise o/w microemulsions and should thus be used for o/w microemulsions. HLB values may be measured by standard techniques.

After having made the initial selection (eg on the basis of HLB), further selection of the surfactant can be achieved by comparing the hydrophobic portion of the surfactant with the structure of the oil, as discussed above. Polar groups on the surfactant also play an important role and should be considered in the matching process.

An alternative or additional surfactant selection system is based on the phase inversion temperature (PIT) and can therefore be referred to as the PIT system. This system

is based upon the temperature at which a surfactant causes an o/w emulsion to invert into a w/o emulsion. It provides information concerning the types of oils, phase volume relationships and the concentration of surfactant which could be used. This system is established on the proposition that the HLB of a nonionic surfactant changes with temperature; the inversion of an emulsion type occurs when the hydrophilic and lipophilic tendencies of the surfactant just balance. No emulsion forms at this temperature. Emulsions stabilised with nonionics tend to be o/w types at low temperatures and w/o types at high temperatures. From the microemulsion standpoint, the PIT system has a useful feature in that it can throw light on the chemical type of surfactant preferred to match a given oil.

Water-miscible formulations as described above include a cosurfactant. Two classes of cosurfactants are normally preferred for use, although others may be used. Aliphatic alcohols (particularly primary aliphatic alcohols) are a first preferred class. They may have a carbon content of from 5 to 12 or more carbon atoms. Lower homologues (for example C<sub>5</sub> to C<sub>7</sub> alcohols) are used to stabilise certain formulations, including w/o microemulsions and alcohols above C<sub>8</sub> (optionally including C<sub>8</sub>) tend to be used to stabilise other formulations, including o/w microemulsions.

Nonionic surfactants form a more versatile group of cosurfactants. They can be balanced with the primary surfactant to give systems that are stable as micellar solutions and as both w/o and o/w microemulsions. A whole range of nonionics can be used, including ethylene oxide propylene oxide block copolymers (as typified by

the PLURONIC PE or PLURIOL PE range from BASF) and alcohol ethoxylates (as typified by the DOBANOL range from Shell). (The words PLURONIC, PLURIOL and DOBANOL are trademarks.)

5 The HLB of the cosurfactant may be less than 12, less than 10, less than 7 or even less than 5. For example, one nonionic cosurfactant is the ethylene oxide propylene oxide block copolymer containing 10% ethylene oxide sold under the trade mark PLURONIC PE 6100 or PLURIOL PE 6100, which has an HLB of 3.0. Other suitable HLB values for cosurfactants are less than 3, for example about 2 or even about 1. PLURIOL PE 3100 has an HLB of 5, and PLURIOL 10100 has an HLB of 1.

15 Choosing an appropriate cosurfactant to be formulated with a surfactant and the other components of microemulsions in accordance with the inventions is possible to one of skill in the art without undue experimentation. The methods previously discussed in relation to the choice of surfactant can also be of assistance in the choice of cosurfactant. Further or in the alternative, the technique of cosurfactant partitioning can be of assistance in the preparation of microemulsions. This approach rests on the premise that the condition responsible for the spontaneous formation and stability of microemulsions came about with a zero (or transiently negative) interfacial tension. The total interfacial tension was given by the formula:

30 
$$\gamma_i = \gamma_{(o/w)} - \pi$$

where:

$\gamma_i$  is the total interfacial tension;

$\gamma_{(o/w)}$  is the interfacial tension before addition of stabilising agents; and

5  $\pi$  is the two dimensional spreading in the monolayer of adsorbed species.

It was then proposed that the initial zero or negative value of the total interfacial tension was the result not so much of a high value of the two dimensional spreading pressure but of the large depression in the value of  
10  $(\gamma_{o/w})_a$ , so that  $\gamma_i = (\gamma_{o/w})_a - \pi$ , where  $(\gamma_{(o/w)})_a$  is the interfacial tension after the addition of stabilising agents.

15 Since most microemulsions appear to form much more readily in the presence of a cosurfactant which is oil soluble, it has been assumed that this material distributed itself between the oil phase and the interface and subsequently changed the composition of the  
20 oil so that its interfacial tension was reduced to  $(\gamma_{o/w})_a$ . This provides a formula with a useful aid to help match emulsifiers (surfactants and cosurfactants) to oils for microemulsification. From an economic standpoint, it is of course desirable only to use a  
25 minimum of cosurfactant which is suitable for use in any formulation of the invention under consideration.

Using the cosurfactant partitioning technique, it has been discovered that for any given surfactant, a short  
30 chain cosurfactant will tend to produce a w/o system, whereas a long chain cosurfactant will tend to promote an o/w system. In the case of soaps, the larger the size of the (hydrated) cation, the more effective that particular soap will be in promoting an o/w microemulsion.

From the point of view of the present invention, it is immaterial whether the zero interfacial argument as a prerequisite for microemulsion stability is correct. The argument has simply been given as an illustration of how the cosurfactant may be selected. It is accepted that the use of the film balance equation is an oversimplification. From the practical formulator's point of view, however, the expression  $(\gamma_{o/w})_a$  can be valuable.

Formulations in accordance with the invention may, but do not have to, contain various other ingredients. For example, a buffering agent (such as potassium hydrogen phthalate) may be present to stabilise the pH of the formulation. Further, a stability enhancer (such as a chloride salt, for example sodium, potassium or calcium chloride) may be present to improve the range of temperature stability (particularly at low temperatures) by reducing the interfacial tension and the droplet size.

The relative proportions of the various ingredients of the formulations in accordance with the present invention can vary widely. For w/o microemulsions, micellar solutions and molecular solutions, broad and preferred ranges of the ingredients may be as follows:

	<u>Ingredient</u>	<u>Broad w/v</u>	<u>Preferred w/v</u>
30	Oil (including dissolved substance if any)	20 to 50%	30. to 40%
	Surfactant	1 to 20%	1 to 5%
	Cosurfactant	1 to 20%	1 to 5%
35	Buffering agent	0 to 2%	0.1 to 1%
	Stability enhancer	0 to 1%	0.05 to 0.5%
40	Water	20 to 70%	50 to 70%

In general the amounts of surfactant and cosurfactant should be kept as low as possible and the amount of water should be kept as high as possible. The above is subject always to the proviso that the total number of percentage parts of the ingredients cannot exceed 100.

For o/w microemulsions, the broad and preferred concentration ranges of the ingredients can be as follows:

	<u>Ingredient</u>	<u>Broad w/v</u>	<u>Preferred w/v</u>
10			
	Oil (including dissolved substance if any)	1 to 20%	1 to 10%
15	Surfactant	1 to 10%	1 to 5%
	Cosurfactant	1 to 10%	1 to 5%
20	Buffering agent	0 to 2%	0.1 to 1%
	Stability enhancer	0 to 1%	0.05 to 0.5%
25	Water	40 to 95%	70 to 90%

Again, the above is subject always to the proviso that the total number of percentage parts of the ingredients cannot exceed 100.

The pests against which the invention protects timber have previously been mentioned and are dictated by the qualitative nature of the pesticidal properties of formulations useful in the invention.

Water-insoluble pesticides can be dissolved in the oil. Cypermethrin, which is a liquid at room or ambient temperatures, can itself constitute the oil, as may any other pesticide which shares this characteristic with cypermethrin.



One synthetic pyrethroid is deltamethrin, which is the common name for 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane carboxylic acid cyano(3-phenoxyphenyl)-methyl ester. Deltamethrin is a potent synthetic pyrethroid pesticide, the preparation of the racemic mixture of which is described in DE-A-2439177. Deltamethrin is insoluble in water, but is soluble in organic solvents such as ethanol, acetone, dioxane, xylene and certain petroleum fractions.

Other synthetic pyrethroids include cypermethrin (3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid cyano(3-phenoxyphenyl)-methyl ester) and permethrin (3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (3-phenoxyphenyl)-methyl ester). Fenvalerate (4-chloro-alpha-(1-methylethyl)benzeneacetic acid cyano(3-phenoxyphenyl)methyl ester) is not strictly speaking a pyrethroid but is generally classed with pyrethroids in the art. Cypermethrin may be prepared as described in DE-A-2326077, permethrin may be prepared as described in DE-A-2437882 and DE-A-2544150, and fenvalerate may be prepared as described in DE-A-2335347. Other pesticides include non-pyrethroid insecticides and acaricides (such as organophosphorus compounds) and fungicides. Organophosphorus compounds include chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate), chlorpyrifos-methyl (O,O-dimethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate), fenitrothion (O,O-dimethyl-O-4-nitro-m-tolyl phosphorothioate) and pirimiphos-methyl (O-2-diethylamino-6-methylpyrimidin-4-yl-O,O-dimethyl phosphorothioate).

Fungicides include carbamates (such as IBPC (3-iodo-2-propynylbutylcarbamate), triazoles (such as propiconazole

(1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl-1H-1,2,4-triazole) and boric acid and its derivatives (such as boron esters).

5 Formulations useful in the invention could, in principle, contain either an insecticide/acaricide or an antifungal (or anti-mould or other agent) or both. In practice, the timber industry tends to pre-treat timber either with fungicide alone or with a combination of insecticide/  
10 acaricide and fungicide, but the invention is not restricted to such preferences.

The amount of active ingredient (or each active ingredient) present in a formulation useful in the  
15 invention will of course depend on its nature. As a guideline, however, insecticide/acaricides will often be present in an amount of from 0.01 to 1% (w/v), preferably from 0.02 to 0.5% and typically from 0.1 to 0.2%, and fungicides will often be present in an amount of from 0.1  
20 to 10% (w/v), preferably from 0.2 to 5% and typically from 0.1 to 0.2%. It should be noted that the invention is not limited to the use of formulations containing only one insecticide/acaricide and/or only one fungicide: a combination of propiconazole and IPBC is popular in the  
25 art, especially in conjunction with permethrin. Propiconazole, IPBC and permethrin are currently the most preferred active ingredients for use in the present invention, alone or in any combination.

30 Concentrated formulations can be prepared. Prior to use in the invention, they will be diluted, for example 5 to 10 fold.

In principle, formulations useful in the invention can be made very simply, by mixing the ingredients. Depending on the thermodynamic favourability of the system, the ingredients will tend to form a microemulsion, micellar solution or molecular solution. In practice, however, kinetic considerations may dictate that some agitation is preferably used to assist the mixing. Agitation may be by magnetic or mechanical means or in some cases ultrasonic.

Once a desired and correctly balanced formulation has been arrived at, it will be found that the order of addition of the ingredients is not normally critical. However, for w/o microemulsions, micellar solutions and molecular solutions, it is preferred to add the ingredients to a vessel in the following order:

1. Add the oil to a vessel
2. Add pesticide dissolved in further oil
3. Add the surfactant and cosurfactant and dissolve them in the oil
4. Add water to give a clear formulation (eg a w/o microemulsion)

Although the above procedure may be found to be suitable for o/w microemulsions, there is a possibility that upon addition of the water, the system could move into the viscoelastic gel region (which can be almost solid) and this could cause practical mixing problems. Consequently, the following procedure is preferred for the preparation of o/w microemulsions:

1. The oil is added to the vessel
2. Pesticide is dissolved in the oil
- 5 3. The surfactant is added and dissolved in the oil
4. Water is added and agitated to give a homogeneous macroemulsion
- 10 5. The cosurfactant is added and the system is agitated to produce a clear o/w microemulsion.

15 Routine modifications, such as the application of heat or altering the degree of agitation can be made to these basic processes to suit the system in use.

20 The invention is not limited by the type of wood or timber that is to be treated. Both hardwood and softwood species and varieties may benefit from it. Pine and spruce are two examples of softwood frequently used in the building trade.

25 Timber is usually pre-treated with pesticide by immersion. According to a second aspect of the invention, therefore, there is provided a method of protecting wood or timber, or an article made therefrom, against pests, the method comprising immersing the wood, timber or article to be protected in a pesticidal formulation which  
30 comprises a microemulsion, micellar solution or molecular solution, whose average particle or droplet size is less than 200 nm.

It is preferred that penetration of the pesticidal formulation into the timber (or wood or article) be aided by the application of a pressure differential. While in principle this can be achieved by applying to timber at atmospheric pressure pesticidal formulation at above atmospheric pressure, it is often better alternatively or additionally to have the timber at below atmospheric pressure immediately prior to applying the pesticidal formulation.

In one embodiment of the invention, timber is housed (for example by being racked) in a chamber, to which a vacuum is applied. The chamber communicates with a reservoir of pesticidal formulation, which is initially prevented from entering the chamber by a suitable valve means. The valve means is then actuated to cause pesticidal formulation to flow from the reservoir into the chamber and to immerse the timber; pressure above atmospheric may be applied to the reservoir to assist with this operation. After a suitable immersion time, the pesticidal formulation is withdrawn from the chamber (for example back to the reservoir). It is then preferred to apply a vacuum to the chamber to take out the last accessible excess formulation.

Immersion or other contact times will be readily determinable by those skilled in the art, depending on the nature of the apparatus used, the pressures and/or vacuums applied, the nature of the wood or timber, the strictures of any appropriate national or other standard and the qualities of the formulations used. Contact times of from 10 seconds to 2 hours for example 1 minute to 90 minutes may be adequate in many circumstances.

Various examples, which illustrate but do not limit the invention, are given below. First, the preparation of the specific formulations used in the examples will be described.

5

### PREPARATIONS

#### Preparation 1

55 litres of an oil-in-water microemulsion was made from the following ingredients:

5

COMPONENT	CONC <sup>N</sup>
Permethrin Tech (96.9%) (Wellcome) <sup>1</sup>	1.09 g.l <sup>-1</sup>
SHELLSOL A	8.00 g.l <sup>-1</sup>
10 PLURONIC PE 10100 <sup>2</sup>	15.00 g.l <sup>-1</sup>
NANSA SSA <sup>3</sup>	10.00 g.l <sup>-1</sup>
Sodium Hydroxide (10% w/w soln)	12.00 g.l <sup>-1</sup>
Calcium Chloride Dihydate (5% w/w soln)	16.00 g.l <sup>-1</sup>
Water (Tap - Ripley, Derbyshire)	962.5 g.l <sup>-1</sup>

15

- 1 96.2% Pure with 25:75 cis:trans ratio
- 2 Ethylene oxide/propylene oxide block copolymer nonionic surfactant
- 3 Alkyl benzene sulphonic acid

20

The permethrin, SHELLSOL A, PLURONIC PE 10100 and NANSA SSA were mixed to give an organic premix. This was then added to an aqueous phase containing all the other components and mixed until clear. The measured pH of the formulation was 4.26. The concentration of the active ingredient is about 1 g/l, and the in-use surfactant concentration is about 25 g/l. The formulation is

25

intended to be used undiluted. The mass distribution mean of the particle sizes, as measured by light scattering at 90° using a Malvern Autosizer IIC instrument at 25°C was less than 25nM.

5

### Preparation 2

Using a similar method of preparation as described in Preparation 1, 30 litres of an o/w formulation having the following ingredients was prepared.

10

Permethrin technical (96.9%)	10.3 g.l <sup>-1</sup>
SHELLSOL A	2.6 g.l <sup>-1</sup>
PLURONIC PE 10100	65.00 g.l <sup>-1</sup>
15 NANSO SSA	35.00 g.l <sup>-1</sup>
Sodium Hydroxide (10% w/w soln)	42.00 g.l <sup>-1</sup>
Calcium Chloride (5% w/w soln)	60.00 g.l <sup>-1</sup>
Water (Tap)	to 1 litre

20 This formulation is intended to be diluted 10% in tap water. After dilution, the surfactant concentration in the working solution will be 10 g/l. The mean particle size is again less than 25nM.

### 25 Preparation 3

Using a similar method of preparation as described in Preparation 1, 30 litres of an o/w formulation having the following ingredients was prepared.

30

Permethrin technical (96.9%)	20.6 g.l <sup>-1</sup>
SHELLSOL A	5.15 g.l <sup>-1</sup>
PLURONIC PE 10100	65.00 g.l <sup>-1</sup>
NANSO SSA	35.00 g.l <sup>-1</sup>

Sodium Hydroxide (10% w/w soln)	42.00 g.l <sup>-1</sup>
Calcium Chloride (5% w/w soln)	60.00 g.l <sup>-1</sup>
Water (Tap)	to 1 litre

- 5 This formulation is intended to be used diluted 5% in tap water. After dilution the surfactant concentration in the working solution will be 5 g/l. The particle size of the formulation is less than 25nM.

10 Control Preparation

1g of permethrin technical (96.9%) was dissolved in 1 litre of white spirits, to serve as a control preparation.

15

Preparation 4

120 litres of an oil-in-water microemulsion was made from the following ingredients:

20

COMPONENT	CONC <sup>N</sup>
Propiconazole <sup>1</sup> (Janssen)	15.28 g.l <sup>-1</sup>
Permethrin <sup>2</sup> (Wellcome)	1.03 g.l <sup>-1</sup>
25 SHELLSOL A	13.37 g.l <sup>-1</sup>
PLURONIC PE 10100	22.50 g.l <sup>-1</sup>
NANSA SSA	22.50 g.l <sup>-1</sup>
Pot. Hydrogen Phthalate	2.50 g.l <sup>-1</sup>
NaOH	2.85 g.l <sup>-1</sup>
30 Water (Tap - Ripley, Derbyshire)	927.70 g.l <sup>-1</sup>

<sup>1</sup> 91.6% Pure

<sup>2</sup> 97% Pure; 25:75 cis:trans ratio



The propiconazole, permethrin, SHELLSOL A and PLURONIC were mixed to create an organic phase. The sodium hydroxide was added to the water; when dissolved, the NANSA was added to the aqueous solution. The pH was adjusted to the range 4.0-4.5. The potassium hydrogen phthalate and organic phase were then added. The formulation is intended to be used undiluted. The mean particle size is 15nm.

#### 10 Preparation 5

2 litres of an oil-in-water microemulsion was made from the following ingredients:

15	COMPONENT	CONC <sup>N</sup>
	IPBC Tech <sup>1</sup> (Troy)	6.2 g.l <sup>-1</sup>
	Pine oil	5.0 g.l <sup>-1</sup>
	SOLVesso 150	36.0 g.l <sup>-1</sup>
20	PLURONIC PE 10100	60.0 g.l <sup>-1</sup>
	NANSA SSA	40.0 g.l <sup>-1</sup>
	NaOH	4.8 g.l <sup>-1</sup>
	KCl	3.5 g.l <sup>-1</sup>
	Water (Distilled)	852.5 g.l <sup>-1</sup>

25

<sup>1</sup> 97% pure

The IPBC was dissolved in the pine oil, SOLVesso 150 and PLURONIC PE 10100. This organic phase was then added to an aqueous phase comprising the water, NANSA SSA, sodium hydroxide and potassium chloride. The resulting preparation was mixed until clear. The formulation is intended to be used undiluted. The mean particle size is 10-20nm.

30

## EXAMPLES

### EXAMPLES 1 TO 3 AND COMPARISON EXAMPLE 1

- 5      Rough (unplaned) pine was supplied by a local builders' merchant in 5 metre lengths (of 50 metre square). These were sawn into 30cm lengths and 6 pieces randomly selected for each test cycle.
- 10     Each of the six pieces of timber was accurately weighed and loaded into a vacuum changer (7 litre capacity) using spaces to ensure free flow of liquid around each piece. 30 litres of treatment liquor were prepared and placed in a polypropylene holding tank. Liquid was transferred to
- 15     the vacuum chamber and then a vacuum of -10mm of Hg was applied and held for 5 minutes. At the end of this time period the pressure was returned to atmospheric and a pump used to increase the pressure in the chamber to 15 psi ( $101 \text{ kN.m}^{-2}$ ). The fluid was maintained at this
- 20     pressure for 5 minutes, at the end of which the fluid was drained out of the chamber back into the holding tank. A vacuum of -20 psi ( $-135 \text{ kN.m}^{-2}$ ) was then applied to the chamber and maintained for 20 minutes. The chamber was then returned to atmospheric pressure and the treated
- 25     timber removed and immediately weighed to determine the uptake of fluid into the wood. The whole process was then repeated a further 19 times with fresh timber using the same sample of treatment liquor.

### 30     EXAMPLE 1

The formulation of Preparation 1 was used in the above procedure. The permethrin uptake into wood, measured as  $\text{g.n}^{-3}$ , was  $21.0 \pm 2.5$  ( $n = 117$ ).

EXAMPLE 2

5 The formulation of Preparation 2 was used in the above procedure. The permethrin uptake into wood, measured as  $\text{g.n}^{-3}$ , was  $21.1 \pm 3.1$  ( $n = 98$ ).

EXAMPLE 3

10 The formulation of Preparation 3 was used in the above procedure. The permethrin uptake into wood, measured as  $\text{g.n}^{-3}$ , was  $20.5 \pm 3.5$  ( $n = 104$ ).

COMPARISON EXAMPLE 1

15 The formulation of the Control Preparation was used in the above procedure. The permethrin uptake into wood, measured as  $\text{g.n}^{-3}$ , was  $18.6 \pm 3.6$ , ( $n = 114$ ).

20 The results shown in Examples 1 to 3 and Comparison Example 1 shows that the invention gives better uptake of permethrin into wood than the conventional white spirits formulation. If the permethrin uptake from white spirits is 100%, the average microemulsion permethrin uptake is 112.2%.

25

EXAMPLE 4 AND COMPARISON EXAMPLE 2

30 Six lengths of timber, three of pine and three of spruce, with a cross-section of 35mm x 35mm, were cut. Each length was further cut into 100mm lengths and numbered sequentially. Alternate pieces were used either for white spirit treatment or treatment in accordance with the invention. All pieces were marked on the same face so that the opposite face could be used for testing.

Both end grains of each sample were sealed by three applications of Evo-Stick wood adhesive, allowing about 2 hours between application. (The expression Evo-Stick is a trademark.) The pine samples were then treated by double vacuum treatment V1 (as defined in BS 5589:1989) and the spruce by V3.

After treatment, samples of wood were extracted using a vertical drill with a 24mm FAUCNER bit. (The word FAUCNER is a trademark.) Dust and shavings were collected from four levels, namely 0 to 1mm, 1 to 2mm, 2 to 3mm and 3 to 4mm. The wood samples were analysed for permethrin by weighing, extracting with hexane, filtering and passing through a 15cm ALPHASIL 5CN HPLC column using a 1% DCM in hexane mobile phase. (The word ALPHASIL is a trademark.) 1 to 5 ppm w/v standards of permethrin in hexane were inserted at regular intervals for calibration.

#### EXAMPLE 4

20

The formulation of Preparation 1 was used in the above methodology, and the average loading of permethrin (% w/w) at the various depths for pine was as follows:

25	0 to 1mm	0.0576%
	1 to 2mm	0.0532%
	2 to 3mm	0.0477%
	3 to 4mm	0.0285%

30 For spruce, the figures were as follows:

	0 to 1mm	0.3167%
	1 to 2mm	0.03565%
	2 to 3mm	0.0152%
35	3 to 4mm	0.0096%

COMPARISON EXAMPLE 2

When the Control Preparation was used in a similar experiment, the permethrin loading figures for pine were as follows:

5	0 to 1mm	0.1398%
	1 to 2mm	0.0423%
	2 to 3mm	0.0184%
10	3 to 4mm	0.0116%

The corresponding figures for spruce were:

	0 to 1mm	0.2363%
15	1 to 2mm	0.0427%
	2 to 3mm	0.0273%
	3 to 4mm	0.0277%

For pine sapwood, the initial layer (0 to 1mm) showed a higher level of permethrin introduced by the conventional formulation, but subsequent layers showed higher levels due to the use of a formulation in accordance with the invention. For spruce sapwood, the trend was the opposite: the 0 to 1mm layer showed higher loadings from the formulation in accordance with the invention, but subsequent layers show higher loadings due to the conventional formulation.

EXAMPLE 5 AND COMPARISON EXAMPLE 3

Pine sapwood samples measuring 200mm in length and having a cross-section in the region of 45mm x 45mm were prepared. The samples were prepared from 12 lengths of planed pine thus giving a total of 24 pieces. Each of

the pine samples was then coded either A or B. The timber samples were then end-sealed with three coats of a 2:1 mixture of ARALDITE PZ820 adhesive and ARALDITE hardener HZ820 prior to impregnation. (The word ARALDITE is a trademark.)

#### EXAMPLE 5

The A samples were subjected to the double vacuum impregnation schedule V1/A (BS 5268: Part 5: 1989, Table 9) and treated with the formulation described in Preparation 1. After treatment, a sample of the sapwood was extracted at a depth of between 2 to 3mm and analysed in order to establish the loading of permethrin present at this depth. The average loading was found to be 0.0452% w/w.

#### COMPARATIVE EXAMPLE 3

The B samples were treated similarly, but with the conventional formulation of the comparative preparation. The average loading of permethrin, under similar conditions of analysis, was found to be 0.0371% w/w.

#### EXAMPLE 6

Over a two month period, beginning early September and ending early November, the effect of long-term recycling of the formulation of Preparation 4 (propiconazole (15.28 g.l<sup>-1</sup>) and permethrin (1.03 g.l<sup>-1</sup>)) was studied in a double vacuum timber impregnation process in accordance with BS5707 Part 1, using treatment schedule reference B1. Each day two separate treatments of an average of twelve pieces of timber (pine) was carried out using the

same sample of Preparation 4 throughout. After each treatment, the formulation was returned to a storage tank ready for the next treatment. For each treatment, the vacuum chamber was charged with fresh timber.

5

The uptake of the formulation was measured each day, the results are shown in Table 1 (unless indicated by the letters "n/d" which stands for "not determined").

10

TABLE 1

TABLE 1: Uptake of Formulation of Preparation 4			
Cycles	Uptake/g	Cycles	Uptake/g
2	39.9	26	67.6
4	41.0	28	53.3
6	32.7	30	52.3
8	61.8	32	n/d
10	n/d	34	42.9
12	n/d	36	66.9
14	52.9	38	66.9
16	63.4	40	54.4
18	51.9	42	44.4
20	-	44	40.3
22	61.8	46	64.3
24	73.2	48	74.7

The uptake averaged  $55.3\text{g} \pm 12.2\text{g}$  (mean  $\pm$  s.d.), indicating no significant change over the period of the test.

30

After certain cycles, the propiconazole concentration, permethrin concentration and pH were measured. The results are shown in Table 2.

TABLE 2

TABLE 2: Formulation Parameters of Preparation 4 during course of Test			
CYCLES	PROPICON. g/litre	PERMETH. g/litre	pH
0	14.93	1.10	4.37
4	14.73	1.10	4.39
12	14.53	1.08	4.39
18	13.88	1.02	4.37
26	13.82	1.03	4.34
40	13.90	1.07	4.40
48	13.95	0.95	4.17
Mean	14.25	1.05	4.35
±	±	±	±
S.D.	0.47 (3.3%)	0.05 (4.8%)	0.08 (1.8%)

The chemical and physical properties of the formulation measured therefore did not significantly alter over the period of the test.

#### EXAMPLE 7

The test methodology used was developed by Timber Division, Building Research Establishment. The methodology has been the subject of various papers (Carey, J.K. and Bravery, A.F. (1988) A technique for assessing the efficacy of preservative envelope treatments applied to wood. International Research Group on Wood Preservation, Document No. IRG/WP/2309 and Carey, J.K. and Bravery, A.F. (1989) A technique for assessing the preventive efficacy against decay fungi of preservative treatments applied to wood. *International biodeterioration* 25, 439-444) and a selection of results have also been published (Carey, J.K. "The preventive effectiveness of preservative treatments against wood-rotting fungi-preliminary results". International



Research Group on Wood Preservation, Document No. IRG/WP/2407. A method which uses similar philosophy has been adopted as a European standard. The test assesses the relative effectiveness of the preservative treatment, as applied, rather than the inherent toxicity of the product. The formulation of Preparation 5 was tested against untreated controls and compared with a reference formulation (1.0% m/m tri n-butyl-tin oxide (TnBTO) in SHELLSOL E<sup>™</sup> solvent). TnBTO is the current industry standard, but concerns are being raised about its safety for continued use.

A series of wood blocks (Scots pine sapwood - *Pinus sylvestris*) is treated with each concentration of the test product, reference preservative or solvent, by brushing at a rate of 1 litre per 4m<sup>2</sup>. After drying, one face of each block is selected as the test face. Holes are drilled into the blocks, from the face opposite the test face, to within 5, 10 and 15mm of the test face. Baits are placed in each hole, in contact with the base. The test blocks (four replicates) are then exposed to attached by basidiomycete fungi, in pure culture, with the test face in contact with a feeder block previously infected with the test fungus. The rate of colonisation from the feeder block, through the treated zone of the test face, is monitored by replacing the baits at regular intervals. The test fungus is recovered from the baits by planting them on a nutrient medium and recording growth. Test fungi used include *Coniophora puteana* BAM 15 (FPRL 11R), *Gloeophyllum trabeum* BAM 109 (FPRL 108N) and *Serpula lacrymans* BAM 315 (FPRL 12E).

The data, in terms of the period of exposure before the test fungus was recovered from a bait installed in each

sampling hole, are presented in Table 3, for each of the test fungi. The data have been summarised in two ways. First, the 'time to first recovery', that is the time until the test fungus is recorded at a particular  
5 detection depth in one of the four replicates. This is indicative of the earliest failure of the treatment, which is regarded as the more significant assessment of performance. Secondly, the 'mean recovery time' has been calculated; that is the mean time for the fungus to be  
10 recovered from the same detection depth in all four replicates. This can be regarded as indicative of the overall performance of the treatment.

TABLE 3

Test treatment	Detection depth - mm	<i>Coniophora puteana</i> BAM 15	<i>Gloeophyllum trabeum</i> BAM 109	<i>Serpula lacrymans</i> BAM 315			
		Time to first recovery	Mean recovery time	Time to first recovery	Mean recovery time	Time to first recovery	Mean recovery time
Untreated	5	4	4.0	4	4.0	6	7.0
	10	4	4.0	4	4.5	8	8.0
	15	4	4.0	4	5.0	8	8.5
1% m/m TnBTO	5	26	> 27.0	22	28.0	ne	
	10	26	> 27.0	20	26.7	ne	
	15	26	> 30.0	20	25.0	ne	
25% test product	5	ne		20**	22.0**	ne	
	10	ne		20**	22.5**	ne	
	15	ne		20**	23.5**	ne	
50% test product	5	ne		12	18.0	ne	
	10	ne		12	18.0	ne	
	15	ne		12	21.5	ne	
75% test product	5	ne		20	26.5	ne	
	10	ne		20	32.0	ne	
	15	ne		22	32.0	ne	
100% test product	5	ne		22	30.0	ne	
	10	ne		22	30.0	ne	
	15	ne		22	30.0	ne	

\* The times are given in weeks

\*\* Affected by contaminating moulds

ne Not established

The untreated controls were all colonised to a depth of 15mm within 4 weeks by the test fungus *Coniophora puteana* and within 6 weeks by *Gloeophyllum trabeum*. These data indicate that these test fungi were very active and capable of aggressively challenging the test treatments. Colonisation by *Serpula lacrymans* was somewhat slower, taking 10 weeks.

With *Coniophora puteana*, the 1% TnBTO reference preservative provided protection against colonisation for at least 26 weeks, which is 22 weeks longer than for the untreated control. All concentrations of the test product provided protection throughout the incubation period of approximately 1 year.

With *Gloeophyllum trabeum* the 1% TnBTO reference preservative provided protection against colonisation for at least 20 weeks, which is 16 weeks longer than for the untreated control. All concentrations of the test product allowed colonisation by the test fungus. Test blocks treated with the 25% concentration became colonised by contaminating moulds during incubation and, for that reason, colonisation by the test fungus appears to have been delayed. Treatment with the 50% concentration provided protection against colonisation for at least 12 weeks. Both 75% and 100% concentrations gave similar results, providing at least 20-22 weeks protection, and therefore have given a performance as good as that of the 1% TnBTO reference preservative.

With *Serpula lacrymans* the 1% TnBTO reference preservative provided protection throughout the incubation period. All concentrations of the test product provided protection throughout the incubation period.

In conclusion, the formulation of Preparation 5 had a significant effect on the rate of colonisation of all the test fungi, particularly *C. puteana* and *S. lacrymans*.

CLAIMS

1. The use of a pesticidal formulation which comprises a microemulsion, micellar solution or molecular solution, whose average particle or droplet size is less than 200 nm, in the pesticidal pre-treatment of timber.
2. A method of protecting wood or timber, or an article made therefrom, against pests, the method comprising immersing the wood, timber or article to be protected in a pesticidal formulation which comprises a microemulsion, micellar solution or molecular solution, whose average particle or droplet size is less than 200 nm.
3. A method or use as claimed in claim 1 or 2, wherein the formulation comprises water, oil, a surfactant and a cosurfactant.
4. A method or use as claimed in claim 3, wherein the oil comprises a hydrocarbon.
5. A method or use as claimed in claim 3 or 4, wherein the surfactant is an anionic surfactant.
6. A method or use as claimed in claim 3, 4 or 5, wherein the anionic surfactant is an alkyl benzene sulphonic acid or salt thereof.
7. A method or use as claimed in any one of claims 3 to 6, wherein the cosurfactant comprises a nonionic surfactant.
8. A method or use as claimed in claim 7, wherein the nonionic surfactant has a hydrophile-lipophile balance (HLB) of less than 12.

9. A method or use as claimed in claim 7 or 8, wherein the nonionic surfactant comprises an ethylene oxide propylene oxide block copolymer.

5 10. A method or use as claimed in any one of claims 3 to 9, wherein one or more pesticides is dissolved in the oil.

10 11. A method or use as claimed in claim 10 where the pesticide comprises a pyrethroid.

12. A method or use as claimed in claim 11, wherein the pyrethroid is permethrin.

15 13. A method or use as claimed in claim 10, 11 or 12, wherein the pesticide comprises a fungicide.

20 14. A method or use as claimed in claim 13, wherein the fungicide is IBPC (3-iodo-2-propynylbutylcarbamate), and/or propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl-1H-1,2,4-triazole).

25 15. A method as claimed in claim 2, wherein penetration of the pesticidal formulation into the timber (or wood or article) be aided by the application of a pressure differential.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00208

**I. CLASSIFICATION OF SUBJECT MATTER** (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A01N25/04; B27K3/34; B27K3/38; B27K3/50

**II. FIELDS SEARCHED**Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int.Cl. 5

A01N ; B27K

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are Included in the Fields Searched<sup>8</sup>**III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>**

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	WO,A,9 003 112 (SHEARD) 5 April 1990	1-11
Y	see page 20; example 1 see claims	12-15
Y	EP,A,0 458 060 (DESOWAG) 27 November 1991 see claims	12-15
Y	EP,A,0 454 431 (TAKEDA CHEMICAL INDUSTRIES) 30 October 1991 see claims	12-15
Y	EP,A,0 385 076 (DESOWAG) 5 September 1990 see claims	12-15
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<sup>10</sup> Special categories of cited documents:<sup>"A"</sup> document defining the general state of the art which is not considered to be of particular relevance<sup>"E"</sup> earlier document but published on or after the international filing date<sup>"L"</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<sup>"O"</sup> document referring to an oral disclosure, use, exhibition or other means<sup>"P"</sup> document published prior to the international filing date but later than the priority date claimed<sup>"T"</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>"X"</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>"Y"</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>"&"</sup> document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

16 APRIL 1993

Date of Mailing of this International Search Report

0 4. 05. 93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DALKAFUKI A.

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 149 051 (BAYER AG) 24 July 1985 ---	
A	FR,A,2 187 226 (THE PROCTER AND GAMBLE COMPANY) 18 January 1974 -----	



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9300208  
SA 69541

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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16/04/93

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